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Indoor air —

Part 38: Determination of amines in indoor and test chamber air — Active sampling on samplers containing phosphoric acid impregnated filters

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Contents

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 6, *Indoor air*.

A list of all parts in the ISO 16000 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

ISO 16000 (all parts) describe general requirements relating to the measurement of indoor air pollutants and the important conditions to be observed before or during the sampling of individual pollutants or groups of pollutants, as well as the measurements procedures themselves.

The definition of indoor environment is given by ISO 16000-1. Dwellings [living rooms, bedrooms, do-it-yourself (DIY) rooms, sport rooms and cellars, kitchens and bathrooms], workrooms or workplaces in buildings which are not subject to health and safety inspections with respect to air pollutants (e.g. offices, salesrooms), public buildings (e.g. restaurants, theatres, cinemas and other meeting rooms) and passenger cabins of motor vehicles and public transportation are among the most important types of indoor environment.

Indoor air —

Part 38:
Determination of amines in indoor and test chamber air — Active sampling on samplers containing phosphoric acid impregnated filters

1 Scope

This document specifies a method for the determination of primary, secondary and tertiary aliphatic and aromatic amines in indoor air using accumulated sampling and high-performance liquid-chromatography (HPLC) coupled with tandem mass spectrometry (MS-MS) or high resolution mass spectrometry (HRMS). It specifies the sampling procedure for determining the mass concentration of amines as mean values by sampling the amines on phosphoric acid impregnated filters. The analytical procedure of the measurement method is covered by ISO 16000-39.

Measurements, performed with samplers containing phosphoric acid-impregnated inert supporting material and operating at specified flow rates for specified sampling periods are described in this document. Requirements regarding sample volume are also defined.

The range of application of this document concerning the concentrations of amines in indoor air depends on the linear range of the calibration line and hence on the gas sample volume (here: from 5 l up to 100 l), the eluate volume (from 1 ml up to 5 ml), the injection volume (from 1 µl up to 10 µl) and the sensitivity of the analytical equipment (e.g. linear range from 2 pg up to 2 ng amine). The range of application can be expected to be from approximately 0,002 µg/m^3 (100 l sample) up to 2 000 µg/m^3 (5 l sample) for a common analytical equipment[1] for the majority of the amines listed in Annex A. The analysis of derivatives of ethanolamine is usually about 10 times more sensitive and the analysis of short-chained aliphatic amines is usually about 10 times less sensitive than the analysis of an average amine.

Although primarily intended for the measurement of amines listed in Annex A, this document can also be used for the measurement of other amines in indoor air.

This document describes procedures for the fabrication and gives requirements for the use of glass tubes containing impregnated filters out of phosphoric acid-impregnated glass wool as samplers, but does not exclude other samplers with proven equal or improved properties. This document also gives procedures for the demonstration of equivalence of other sampler types or methods.

This document does not cover the determination of amines in other media like water or soil. Furthermore, it does not cover the determination of isocyanates in indoor air as corresponding amines (covered by ISO 17734-1 and ISO 17734-2). Quaternary amines are also not included in this document.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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[1] Waters “TQ-D” is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO online browsing platform: available at https://www.iso.org/odp
- IEC Electropedia: available at https://www.elctropedia.org/

3.1

amines

nitrogen containing compounds with a sufficient vapor pressure (>10^{-3} Pa) and a free electron pair at the nitrogen atom which can be protonated by phosphoric acid

4 Amines in indoor air

4.1 Properties of amines

Amines are basic and polar substances.

There are primary, secondary, tertiary, and quaternary amines.

Quaternary amines are not included in this document as they have no free electron pair and therefore have very different properties. In this document, the term “amines” includes primary, secondary, and tertiary amines only.

Not protonated amines are oxidation sensitive.

The reaction of amines with acids results in ammonium salts of the amines. The ammonium salts are not oxidation sensitive.

4.2 Origin and occurrence of amines in indoor air

Amines are produced by technical chemical processes and processing and in addition by biotic or abiotic decomposition of nitrogen compounds. Besides sources of biological origin, indoor air sources of amines could be, for instance, products containing polyurethane, especially foams, such as in vehicle seats, mattresses, pillows, and upholstered furniture or as thermal insulation or sound absorbing material. Several amines, in particular aromatic amines, are known as harmful compounds. Furthermore, most amines have an unacceptable odour in combination with a low odour threshold.

Further sources are for example food, such as fish (aliphatic amines) and cigarette smoke (aromatic amines).

5 Sampling strategy — Measurement procedure

5.1 Structure and properties of the samplers

The basic structure of an amine sampler for active sampling consists of a container, preferably a glass or plastic tube, and a filter. The filter is impregnated with an acid with low vapour pressure and without an oxidizing effect. In this regard, phosphoric acid is most suitable. The filter material itself shall be inert, such as untreated glass wool, glass spheres or glass frits. Basically, the inert filter material could be a porous, inert polymer.

The suggested sampler consists of a glass tube with 6,25 mm outside diameter on a length of 60 mm, and a tapering on a length of 20 mm with an outside diameter of the tip of 2,5 mm. The suggested filter consists of 50 mg of untreated glass wool impregnated with approximately 100 µmol or 9,8 mg H_3PO_4, respectively.

The sampler that is described as an example in this document (see 5.2) is handmade.

Until now, no verified commercially available amine samplers for active sampling are known.

Alternative samplers shall be tested by the procedure described in 5.9.

5.2 Manufacturing of the samplers

5.2.1 General

The manufacturing of active samplers with phosphoric acid impregnated glass wool is described in the following:

Chemical agents:	470 µl phosphoric acid 85 % (density = 1,685 g/cm^3)
	200 ml acetonitrile
	2,5 g untreated glass wool
Laboratory equipment:	500 ml round bottom flask
	Glass tubes (6,25 mm outside diameter on a length of 60 mm, tapering on a length of 20 mm with an outside diameter of the tip of 2,5 mm)
	Rotary evaporator
	1 000 µl automatic pipette

5.2.2 Implementation

Approximately 100 ml acetonitrile are filled into a 200 ml volumetric flask. Then 470 µl phosphoric acid 85 % are filled into the flask and mixed with the acetonitrile. After that, the flask is filled up to the 200 ml mark with acetonitrile and the solution is mixed again to get a 34,3 mmol/l H_3PO_4 solution in acetonitrile.

2,5 g glass wool is transferred into a 500 ml round bottom flask together with 200 ml 34,3 mmol/l H_3PO_4 solution in acetonitrile. (2,74 mmol H_3PO_4/g glass wool).

The acetonitrile is distilled off in a rotary evaporator at 100 r/min and at a temperature of 90 °C to 100 °C.

Each glass tube is packed with (50,0 ± 0,5) mg of the resulting impregnated glass wool (corresponds to 137 µmol H_3PO_4/sampler if all H_3PO_4 remains on the glass wool and if the acid is equally distributed). The impregnated glass wool is compressed thoroughly in the glass tube. Both opening of the glass tube are sealed by suitable plastic caps.

Until application, the samplers are stored in the freezer at −36 °C.

5.2.3 Verification

The mass of phosphoric acid on each sampler (approximately 9,8 mg or 100 µmol, respectively) is verified by titrating 5 samplers for each batch (10 % of the batch) with a 0,01 molar aqueous solution of sodium hydroxide and phenolphthalein as an indicator. The change of colour corresponds to the second equivalence point (complies with approximately 20 ml 0,01 M NaOH solution).

$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$

$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$ (transition of the indicator from colourless to purple)

____

$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$

Due to inhomogeneities (and losses) there are variations in the amount of H_3PO_4 on the samplers. Acceptable are (100 ± 50) µmol H_3PO_4/sampler which corresponds to (20 ± 10) ml 0,01 M NaOH solution. The batch (the other 45 samplers) can be used if all five titrated samplers are within this range.

5.3 Selection of the suitable sampling time

The sampling volume depends on the expected concentration of amines in the sample air. It should be between 5 l and 100 l. Suggested sample volumes and sampling times are summarized in Table 1.

Table 1 — Suggested sample volumes and sampling times

Lowest expected concentration µg/m³	Highest expected concentration µg/m³	Suggested (uncorrected) sample volume l	Corresponding sampling time min
1	100	5	5
0,5	50	10	10
0,1	10	50	50
0,05	5	100	100

During sampling, the humidity of the sampled air should be lower than 60 % RH (relevant is the temperature and the humidity in the sampler) to avoid water condensation in the sampler.

5.4 Sampling protocol

The sampling protocol should contain at least following aspects:

- measurement objective (short description);
- status review (description, if necessary detailed);
- initial of operator;
- date and time of measurement;
- sample number;
- sampling time (min);
- sampling volume (l);
- indoor climate conditions: pressure (hPa), temperature (°C), relative humidity (% RH);
- flow conditions in the room (if appropriate, in a drawing);
- intake point (if appropriate marked in a drawing);
- colour of the indicator paper wetted with the eluate remained in the glass wool of the sampler after eluting (see 5.8);
- colour of the indicator paper wetted with the eluate from the tip of the Pasteur pipette after transferring the eluate from the volumetric flask to the vial (see 5.8).

5.5 Comparative measurements

Due to the lack of pertinent evaluation criteria concerning amine concentrations in indoor air, a comparison by means of parallel measurements either with the situation in another room (e.g. without recently implemented material like sound absorbing material, thermal insulation or upholstered furniture) or with the outdoor air concentration can be helpful.

If appropriate, additional comparative samples (which can later be analysed only if necessary) should be taken as a precaution.

5.6 Sampling procedure

Prior to sampling, the required samplers are taken out of the freezer and stored at room temperature until thermal equilibrium to avoid condensation of water on the filter. Before sampling, the sealing caps on both sides of the samplers are removed. If applicable, the tip of the sampler is connected to the test chamber by a suitable short flexible hose. The sampler end with 6,25 mm diameter is connected to a suitable flexible hose that is connected with a calibrated sampling pump.

The sample air flow is adjusted to at most 1 l/min, usually to approximately 1 l/min. The sampling volume depends on the expected concentration of amines in the sample air. It should be between 5 l and100 l. Usually, 50 l is used as standard sampling volume.

The samples shall be labelled indicating at least sample number, date and time of sampling, and initials of the operator. The label should be fixed on the sampling tube and not on the sealing caps.

5.7 Storing of the samples

After the sampling is completed, both ends of the sampler are sealed with the sealing caps and the loaded samplers are stored in a freezer at −36 °C until sample preparation. They can be stored this way up to 6 months.

5.8 Sample preparation and transfer to the analytical procedure

The sample preparation is done by eluting the phosphoric acid and the corresponding ammonium salts of the amines with water.

a) Both sealing caps are removed from the sampler tubes.

b) The samplers are plugged into a 5 ml volumetric flask (with the tip at the bottom and the wide opening at the top).

c) The elution of the amines or the corresponding ammonium salts, respectively, is done by an automatic pipette with 5 000 µl water (HPLC quality). The water is carefully supplied onto the impregnated glass wool from the side of the wide tube opening.

d) The water flow through the sampler tube take place drop wise. If necessary, the dropping rate can be accelerated by slightly lifting the sampler tube from the volumetric flask. The flow from the top to the bottom should be slow and constant. Mixing of the liquid in the tube shall be avoided (especially when the elution volume is reduced to 1 ml). It is desired that the water at the bottom dissolves the ammonium salts — as well as the phosphoric acid — and washes them into the volumetric flask while the water at the top should stay free of phosphoric acid and ammonium salts.

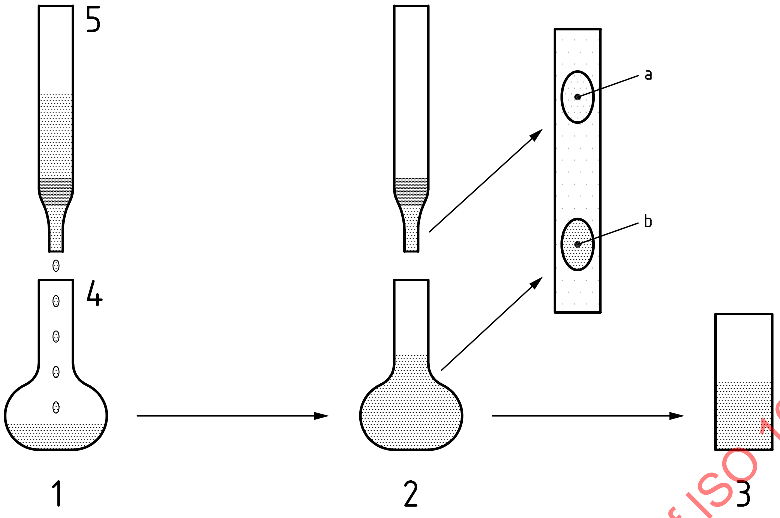
e) The sampler tubes remain on the volumetric flask until the whole water passed through the sampler. If necessary, add some drops of water to fill up the volumetric flask to the 5 ml mark.

f) The aqueous sample solutions are sucked out of the volumetric flasks by long Pasteur pipettes and transferred into clean vials for the high-performance liquid chromatography. The vials are sealed with crimp caps and are stored in the refrigerator at 4 °C until they are analysed (for details, see ISO 16000-39).

g) The last drops of water from the samplers are dropped onto Congo red indicator paper. The red colour shall remain without changing because a changing of colour to blue would indicate that not all phosphoric acid, and therefore potentially not all amines, are transferred into the volumetric flask.

h) Likewise, residues of the sample solution in the Pasteur pipettes (used for the transfer to the vials) are pressed out onto Congo red indicator paper by means of a rubber cap. The indicator paper shall turn deeply blue. The blue colour indicates that the eluate is acidic and that the sampler was not overloaded.

The last two steps are illustrated schematically in Figure 1.



Key

1	elution with water
2	test of the eluate with Congo red indicator paper
3	eluate in a vial for HPLC-MS-MS
4	volumetric flask
5	sampler
a	Neutral.
b	Acidic (deeply blue colour).

Figure 1 — Scheme of testing of the residues of sample solution and of the residues of the samplers

5.9 Demonstration of equivalence of other sampler types or methods

The amine samplers described in 5.2 were successfully tested and used for the sampling of the amines listed in Annex A. Other types of phosphoric acid impregnated filters can be used as an alternative when the capability and performance of these samplers are demonstrated by a chamber test which is described in the following:

For the testing of the suitability of the samplers, it is necessary to generate an air sample with a known concentration of analytes/amines. This can be done using an emission test chamber with a clearly defined gas volume flow (in the range of 1,5 m^3/h up to 3,0 m^3/h or 25 l/min up to 50 l/min, respectively) and vials (e.g. 1,5 ml) filled with certain amines (Table 2; pure, not as a solution) and closed with evaporation/diffusion barriers (Table 2). The diffusion barrier shall be adjusted for each amine to the gas volume flow of the emission test chamber. By measuring the mass loss of the vials, the concentration in the air can be calculated as shown in Formula (1):

$$\left(\frac{\Delta m}{\Delta t}\cdot 1\,000\ \mu\text{g/mg}\right):\left(\Delta V/\Delta t\right)=\frac{\Delta m}{\Delta V}=c \qquad (1)$$